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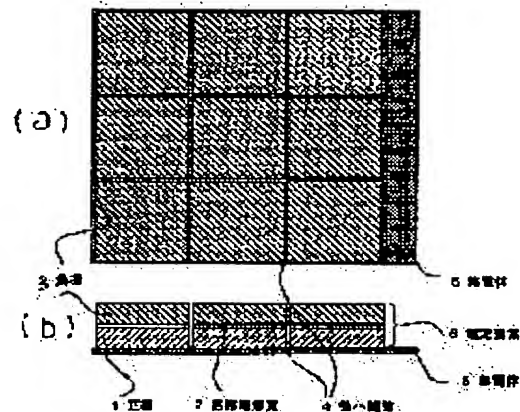
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(54) FULLY SOLID SECONDARY BATTERY AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To improve charge/discharge cycle characteristics and to maintain high energy density by preventing the characteristics from being deteriorated due to expansion/contraction of electrodes or their brittle fracture by shock.

SOLUTION: This fully solid secondary battery has a plurality of battery elements 6 disposed on a current collector and each made by layering a positive electrode 1 made of an inorganic compound, a solid electrolyte 2, and a negative electrode 3. The plurality of battery elements 6 are disposed at spaces of 0.1 to 5000 μm , or the plurality of battery elements 6 are disposed at spaces not more than 5% of the total disposition width of the battery elements 6. The area of each battery element 6 is 1 μm^2 to 100 cm^2 .



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CLAIMS

[Claim(s)]

[Claim 1] All the solid-state rechargeable batteries characterized by arranging said two or more cell elements with a 0.1-5000-micrometer gap in all the solid-state rechargeable batteries that arranged two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and prepared it on the charge collector.

[Claim 2] All the solid-state rechargeable batteries characterized by arranging said two or more cell elements with 5% or less of gap of the total arrangement width of face of this cell element in all the solid-state rechargeable batteries that arranged two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and prepared it on the charge collector.

[Claim 3] each area of said cell element -- 1micrometer² -100cm² it is -- all solid-state rechargeable batteries according to claim 1 or 2 characterized by things.

[Claim 4] The manufacture approach of all the solid-state rechargeable batteries characterized by cutting this cell element to plurality combining dicing, laser abb RESSHON, chemical etching, plasma etching, ion etching, an electron ray, or these in the manufacture approach of all solid-state rechargeable batteries of preparing two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and formed it on a charge collector after forming a cell element on said charge collector.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to all the solid-state rechargeable batteries that prepared two or more cell elements especially on the charge collector about all solid-state rechargeable batteries.

[0002]

[Description of the Prior Art] Conventionally, as an electrolyte of various cells, although the electrolytic solution of a drainage system or a non-drainage system was generally used, with the demand of thin-shape-izing of the various electronic application devices represented by portable information terminal equipments, such as video photography equipment, a notebook computer, or a cellular phone, and a lightweight miniaturization, it replaces with the above liquefied electrolytes and the solid electrolyte cell using the gel electrolyte which consisted of polymeric materials attracts attention in recent years. Moreover, the various proposals also of the solid electrolyte cell using the inorganic solid electrolyte and the solid polymer electrolyte as an electrolyte are made. By these cells, although it is a solid-state therefore, thin shape-ization is attained by the approach of spreading, a laminating, etc., and positive loading to a pocket device is achieved. Furthermore, all the solid-state rechargeable batteries that formed the electrode active material and the electrolyte with the inorganic compound are also advocated as what can employ efficiently the merit that safety is high and the temperature use range can be taken extensively.

[0003] However, in these all solid-state rechargeable battery, it is fundamentally inherent in the problem of the crack in the electrode which is a sintered compact, or the solid electrolyte which is similarly a sintered compact, i.e., the problem of a brittle fracture. That is, although it is all the solid state batteries that made the inorganic compound sinter therefore, the destruction accompanying expansion contraction of charge and discharge and the destruction accompanying an impact occur. Once a crack arises in large area electrode or solid electrolyte, destruction advances with the generating part as the starting point, soon, destruction will attain to all the whole solid state batteries, and the whole ***** or the whole solid electrolyte ***** will pose a problem with the fatal crack in all solid state batteries.

[0004] Until now, in the rechargeable lithium-ion battery, the device of the relief valve which controls the structure of preventing destruction of sheathing in order to prevent the destruction and breakage, and the run away reaction which occurred inside the cell is advocated. Moreover, also when a cell is damaged completely, the defense mechanism for securing the insurance etc. is advocated. However, about the prevention device of the structure destruction inside a cell, it did not consider as a problem. Moreover, improvement of the active material itself, examination of the mixed ratio of the active material with which expansion contraction differs or examination of the adaptation material to a cell structural member, etc. was performed so that the problem about expansion contraction of the active material accompanying charge and discharge might be seen by JP,5-82131,A, JP,5-159803,A, or JP,6-338321,A as a cure in the system which used nonaqueous electrolyte. And although arranging and producing the septum containing an insulator between the cell elements of all solid-state rechargeable batteries was proposed (for example,

refer to JP,5-283055,A and JP,6-215753,A), all were insufficient as a solution over the performance degradation of all the solid-state rechargeable batteries by destruction of a cell element, and there was no protection about the destructive mode of all solid-state rechargeable batteries.

[0005] Like JP,7-122279,A on the other hand, in a solid state battery or a set cell, since the design which establishes space in the interior of a cell is what is a thing aiming at the workability improvement in the cell which needs terminal strapping etc., or brings about flexibility in order to give cell voltage or the design degree of freedom of capacity by giving wiring on manufacture etc. in the interior of a cell, it is inadequate too from the point of the improvement in energy density. That is, in order to carry to a device or to raise productivity, such a configuration had to be taken, and since many parts which do not contribute to the energy density of a cell directly were included, thing sufficient as energy density was not able to be obtained.

[0006] Therefore, this conventional cell is insufficient as a cell element which does not lower degradation or energy density by destruction.

[0007] It is in this invention being made in view of the above-mentioned trouble, and that 1st purpose preventing property degradation of the cell produced by the brittle fracture by expansion contraction and the impact of the electrode of all solid-state rechargeable batteries, and raising a charge-and-discharge cycle property, and it is in maintaining a high energy consistency in the energy density of a cell as the 2nd purpose, attaining this 1st purpose.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, all the solid-state rechargeable batteries of this invention arranged said two or more cell elements with the 0.1-5000-micrometer gap in all the solid-state rechargeable batteries that arranged two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and prepared it on the charge collector.

[0009] Moreover, in all the solid-state rechargeable batteries that arranged two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and prepared it on the charge collector, said two or more cell elements were arranged with 5% or less of gap of the total arrangement width of face of this cell element.

[0010] the above-mentioned solid-state rechargeable battery -- each area of said cell element -- 1micrometer² -100cm² it is -- things are desirable.

[0011] Furthermore, by the manufacture approach of all the solid-state rechargeable batteries of this invention, in the manufacture approach of all solid-state rechargeable batteries of preparing two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and formed it on a charge collector, after forming a cell element on said charge collector, this cell element is cut to plurality combining dicing, laser abb RESSHON, chemical etching, plasma etching, ion etching, an electron ray, or these.

[0012] [Function] It is possible to stop the brittle fracture caused with the expansion contraction which all solid state batteries have on the charge collector of all solid state batteries when two or more cell elements are arranged with a very small gap, or an impact in each cell element. Moreover, since the gap is very small, even when it constitutes from many cell elements, it cannot reduce the energy density per the area, that is, can stop the non-donor product to a charge-and-discharge reaction to the minimum, and can form the cell of a high energy consistency.

[0013]

[Embodiment of the Invention] Hereafter, this invention is explained using drawing. The configuration of the cell element in [all] a solid-state rechargeable battery is shown in drawing 1 . The cell element used as the structure into which this inserted the solid electrolyte 2 with the positive electrode 1 and negative electrode 3 of a pair is arranged on the charge collector 5 with the very small clearance 4.

[0014] A positive electrode 1, a negative electrode 3, and a solid electrolyte 2 consist of

ingredients shown below, respectively. Namely, as for the active material as an ingredient of electrodes 1 and 3, the chalcogen ghost of transition metals and the transition-metals oxide of Spinel structure are raised. As a chalcogen ghost, TiO_2 , Cr_2O_3 , and V_2O_5 , MnO_2 and CoO_2 An oxide, sulfides, such as TiS_2 , and VS_2 , FeS , etc. are raised. etc. -- further -- as Spinel structure -- LiMn_2O_4 the various transition-metals oxides represented and the part of those -- various transition-metals oxides, such as an element permutation mold oxide and $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and the part of those -- an element permutation mold oxide can be used. However, from a viewpoint of the stability of the active material which relates to the cycle engine performance of a cell directly, the active material ingredient of an oxide system is desirable as an active material.

[0015] It is using for a negative electrode 3, respectively what shows more **** potential to a positive electrode 1 for what is not limited especially concerning the selection, compares the charge and discharge potential of two kinds of transition-metals oxides, or a sulfide, and shows electropositive potential more, when using these ingredients as the active material of a positive electrode 1, or an active material of a negative electrode 3, and it is possible to constitute a thing with the cell voltage of arbitration. Furthermore, the need is accepted from the purpose of electronic conductivity assistance, and it is SnO_2 . TiO_2 The said conductive additive is mixed and it considers as an electrode material.

[0016] moreover -- the inorganic solid electrolyte 2 used by this invention -- $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [for example,] $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ etc. -- a crystalline substance solid electrolyte -- $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5-40\text{Li}_2\text{O}-30\text{LiI}-35\text{B}_2\text{O}_3-25\text{LiNbO}_3$, Oxide system noncrystalline solid electrolytes, such as $10\text{Li}_2\text{O}-25\text{B}_2\text{O}_3-15\text{SiO}_2-50\text{ZnO}$, $45\text{LiI}-37\text{Li}_2\text{S}-18\text{P}_2\text{S}_5$ and $1\text{Li}_3\text{PO}_4-63\text{Li}_2\text{S}-36\text{SiS}_2$ etc., although a sulfide system noncrystalline solid electrolyte etc. can be used It is more desirable to use an oxide system ingredient from the standpoint of the stability of an active material in respect of maintenance of cycle charge/discharge capability ability.

[0017] Next, arrangement of the cell element 6 to a charge collector 5 top is explained. The laminating of each cell element 6 is carried out on the charge collector 5 with the ingredient mentioned above. It forms by production of a laminated structure being able to form each electrode layer and a solid electrolyte layer by screen-stencil of a up to [sheet forming or a charge collector], making the formed layered product sinter with pressurization heating by the hotpress, and carrying out eburnation. After drying the sheet obtained after applying to the thickness which needs the paste of each electrodes 1 and 3 and a solid electrolyte 2 first with screen-stencil or a doctor blade method in the case of the former sheet forming, it degreases by drying on both sides of a solid electrolyte 2 by the positive/negative two electrodes 1 and 3, and the cell element 6 is produced with a hotpress. furthermore, this production -- a positive electrode 1, the negative electrode 3, and a solid electrolyte 2 -- it is also possible to produce all by screen-stencil or sputtering under an inert atmosphere.

[0018] Similarly the electrode paste carried out with ** forms a solid electrolyte 2 by printing, after performing desiccation and cleaning. Printing and desiccation cleaning of an electrode are further performed after desiccation and cleaning. The cell element 6 is made to sinter with a hotpress first. Then, junction formation of the charge collector 5 is carried out. As a charge collector 5, foils, such as aluminum, gold, nickel, or titanium, can be used.

[0019] Accumulation of the cell element 6 to a charge collector 5 top is producible by calcinating with a hotpress too under an inert atmosphere, or joining with a paste, after installing the cell element 6 produced by the above-mentioned approach to up to a charge collector 5. Moreover, it is also possible to process the configuration and gap which each cell element 6 needs, and to form in them on a charge collector 5, in the electrode of the large area produced by each method of creating previous, with either of the approaches, such as dicing, laser abb RESSHON, chemical etching, plasma etching, ion etching, and an electron ray. Although the gap width of face of processing is producible by any technique as a design, what was especially produced by dicing or laser abb RESSHON is the optimal also in the production configuration and property.

[0020] Moreover, it has a 0.1-5000-micrometer clearance between the cell elements 6. It is impossible in practice from processing being difficult in a gap smaller than 0.1 micrometers. Moreover, it is not realistic too to arrange exceeding 5% to the width of face of the thing and the

cell element 6 exceeding 5000 micrometers, when a deployment of a spatial body product is considered. Therefore, as width of face for lowering neither the inter-electrode short circuit prevention after processing, nor energy density, it must be the range of 0.5-1000 micrometers. [0021] Moreover, as an area of the cell element 6, it is 2 1 micrometer 2-100cm from the absolute magnitude regulated by the precision list of processing from expansion contraction of a crystal. As an area which can use energy effectively from the optimal gap width of face although the range is suitable, it is 2 4 micrometers 2-40cm. It is desirable that it is the range.

[0022] thus, the set cell which carried out accumulation arrangement constitutes a parallel circuit from on the same charge collector, and it becomes possible also for an appearance top and the actual condition the same to operate it as all the solid-state rechargeable batteries of a large area. Therefore, charge-and-discharge actuation whose ***** the charge and discharge current as the aggregate of the cell element 6 according to individual does not have as a cell capacity of all large area independent solid-state rechargeable batteries, either is carried out.

[0023] As shown in drawing 2, all the solid-state rechargeable batteries that used these cell element 6 processed the positive/negative charge collector, formed the terminal electrodes 7 and 8, and have taken the gestalt covered or packed up by the insulating sheathing 9. Enclosure by thermocompression bonding and covering by resin mold are performed using the laminating complex film of high polymer films, such as polyethylene, polypropylene, or polyester, and aluminum foil as sheathing.

[0024]

[Example] Next, below, as the solid-state rechargeable battery of this invention was explained in full detail below, it was evaluated.

[0025] (Example 1)

It formed like <sample 1-1> each cell element. It is Li [Li_{0.1} Mn_{1.9}] O₄ as positive active material. It used. as a start raw material -- MnO₂ receiving -- Li₂ CO₃ etc. -- the compound was mixed so that it might become the Li:Mn predetermined mole ratio 1:1.9, and it compounded by calcinating in atmospheric air at 450 degrees C - 750 degrees C. It is 30Li-41Li₂ O-29P₂ O₅ as an inorganic solid electrolyte to 75 % of the weight of this active material. As 15 % of the weight and a conductive auxiliary, weighing capacity of the 10 % of the weight was carried out for ITO (In₂ O₃:SnO₂ = 95:5), and fine particles were fully mixed. The polyvinyl butyral was added 5 % of the weight outside as a binder for shaping to these mixed fine particles, and the paste was prepared for toluene to the solvent using the ball mill. After fabricating the prepared paste in thickness of 100 micrometers and vaporizing a solvent, cleaning of a binder was performed at 350 degrees C, and the electrode was produced through baking in 650-degree C atmospheric air.

[0026] On the other hand, it is Li₁/Li [3 Ti₅/3] O₄ as a negative-electrode active material. It used. as a start raw material -- TiO₂ receiving -- Li₂ CO₃ etc. -- the compound was mixed so that it might become the Li:Ti predetermined mole ratio 4:5, and it compounded by calcinating among atmospheric air at 650-950 degrees C. This negative-electrode active material is used and it is inorganic solid electrolyte 30Li-41Li₂ O-29P₂ O₅ to 85 % of the weight of active materials as well as a positive electrode. Fine particles were mixed at 15% of the weight of a rate, and negative-electrode mixing fine particles were produced. The binder as well as [as a binder for shaping] a positive electrode was added 5 % of the weight outside to these negative-electrode mixing fine particles, and the paste was prepared for toluene to the solvent using the ball mill. After fabricating the prepared paste in thickness of 80 micrometers and vaporizing a solvent, cleaning and baking of a binder were carried out like the positive electrode, and the electrode was produced.

[0027] Moreover, solid electrolyte 10Li₂ O-25 B-2 O₃-15SiO₂-50ZnO was mixed by the weight ratio 80:20 to the above-mentioned solid electrolyte, 5 weight sections addition of the binder was carried out like the electrode, toluene was used for the solvent, and the paste was prepared. Laminating spreading of the prepared paste was carried out by the thickness of 20 micrometers by screen-stencil on the positive-electrode baking electrode. After carrying out desiccation vaporization of the solvent after applying, degreasing a binder at 350 degrees C among atmospheric air and making three layers into one for a negative-electrode baking object in piles,

it is 300 – 600 kgf/cm² with a hotpress. Pressurization baking was carried out at 450–700 degrees C with the pressure. Fabrication of the cell element was carried out to 30mmx30mm by this approach. Between cell elements, accumulation arrangement is carried out to up to the charge collector aluminum of 100mm angle in a 0.5mm gap, similarly nine cell elements produced as shown in drawing 3 are pinched with the charge collector of 100mm angle, and they are 400–600 degrees C and 200 – 600 kgf/cm² under an inert atmosphere. It connected with the charge collector with the hotpress on conditions. The terminal processed the configuration of a terminal and took out charge collector aluminium foil. The insulation of a charge collector was performed by inserting a resin film. An aluminum lamination is used as sheathing and it is a dew-point. – The cell element was enclosed by thermocompression bonding under the 45-degree C desiccation ambient atmosphere, and ten cels of all solid-state rechargeable batteries were produced.

[0028] The rechargeable battery charging and discharging device performed charge-and-discharge characterization of a cell. After it charged all solid state batteries to 3.5V with the current of 50microA as charge conditions and the electrical potential difference reached 3.5V, charge was suspended and it held for 5 minutes, and after that, it discharged by the discharge current of 50microA to the electrical potential difference of 1.0V, discharge was suspended, it held for 5 minutes, and the charge-and-discharge cycle trial by the repeat of charging to 3.5V was performed again. Five cels were followed in evaluation of the cell engine performance by transition for every cycle of discharge capacity.

[0029] Furthermore, about the five remaining cels produced on the same conditions, whenever it performed 25 cycle charge and discharge, the drop test to the floor line of concrete was performed by making into one unit combination of the direction of the 6th page of the cell which showed all solid-state rechargeable batteries to drawing 3 from height of 50cm. Five every units each of drop tests were performed.

[0030] One cell element was produced to 90mmx90mm by the approach shown by the <comparison sample 1-1> sample 1-1. Similarly ten cels of all solid-state rechargeable batteries equipped with a terminal and sheathing for this cell element like the example 1 were produced. Five cels performed charge-and-discharge cycle measurement like the example, and remainder 5 cel performed the same drop test every 25 cycles. The cycle characteristic test result of a sample 1-1 and the comparison sample 1-1 is shown in drawing 4.

[0031] a sample 1-1 and the comparison sample 1-1 -- in 25 cycle, it was checked both the first stage that the almost same cycle capacitance characteristics are shown. However, although capacity degradation advanced rapidly in the example of a comparison when it went through 150 cycle charge and discharge, as for such degradation, samples 1 and 2 did not happen.

[0032] This is making a cell element small and is because it becomes possible to stop the absolute magnitude of the expansion contraction for every cell element, so decline in the utilization factor inside an electrode is controlled. When the electrode after cycle progress was inspected, peeling of a charge collector perimeter and an electrode was checked in the comparison sample 1. Moreover, when the electrode surface was ground, much particle desorption at the time of nebula or polish was checked by the core and the periphery within the electrode surface, and growth of the defect inside the electrode active material accompanying charge and discharge was supported. The result of a drop test is shown in drawing 5.

[0033] In all the solid state batteries shown in the sample 1-1, capacity degradation by fall was hardly seen. However, by the cell which consisted of one cell element produced by the comparison sample 1-1, what shows extreme capacity degradation from immediately after fall of five units of 25 cycle eye has appeared.

[0034] And by the comparison sample 1-1, the inclination of capacity degradation in the middle of a cycle is also large, and is conjectured that the whole electrode has deteriorated by the charge-and-discharge cycle with the defect as the starting point produced in fall.

[0035] When the cell after a charge-and-discharge cycle was disassembled, in the case of the comparison sample 1-1, compared with the cycle trial which does not fall, much cracks were able to be checked by the result of the cycle trial including fall. Moreover, in the sample 1-1, although there were some which can check much cracks to some cell elements, the crack was not accepted in the other cell element. In order that the defect of a crack with a very small cell

element might be shut up in each cell element and might not spread from this to other cell elements by minding a very small clearance, it was checked that the cycle engine performance of all the whole solid state batteries is maintainable.

[0036] As compared with one 90mmx90mm large area, it is clear that the cross section's of all the solid-state rechargeable batteries at the time of being accumulated in the gap exceeding 1.5mm which is 30mm of 5% of cell elements about a cell gap on the other hand energy density carries out 6% or more of fall, and it excepted in the exam.

[0037] (Example 2)

The 30mmx30mm cell element was produced like the <sample 2-1> example 1-1, and ten cels of all solid state batteries too accumulated four cels on up to the charge collector like the example 1 in the 0.5mm gap were produced.

[0038] The 35mmx35mm cell element was produced like the <comparison sample 2-1> sample 2-1, and ten cels of all solid state batteries that accumulated three cels on up to the charge collector like the example 1 in the 0.5mm gap were produced.

[0039] The comparison sample 1 performed the charge-and-discharge cycle trial in the above-mentioned sample 1 list like the example 1. A result is shown in drawing 6.

[0040] By the charge and discharge test to 400 cycles, the capacity is falling to a maximum of about 60% from initial capacity in the comparison sample 2-1 by the sample 2-1 to the capacity variability region being only 80% in an initial capacity factor. Since the area of the cell element to constitute is large about 30%, this is because degradation accelerated more by destruction of the cell element by the expansion contraction accompanying charge and discharge.

[0041] (Example 3)

The cell element which consists of one 90mmx90mm piece like the <sample 3-1> comparison sample 1-1 was produced. The electrode side was fixed to up to a charge collector by heating and pressurization like [while] the example 1. This electrode was fixed in the processing chamber in an atmospheric-air air current, and the electrode by the YAG laser was processed. In processing, they are power density 1 - 106 J/cm². The rate to which the cell element on an X-Y stage is moved was adjusted using the YAG laser of an output, and micro processing was performed. Processing width of face was adjusted with the focus of laser, and processed 9 ****s of cell elements equally. Since laser light reflected in respect of charge collector aluminum, it was able to leave only the charge collector and was able to be processed. It checked after processing that processing width of face was 2-8 micrometers by microscope observation.

[0042] The charge collector was further attached in the cell element after this processing for the charge collector using heating and pressing, or a commercial conductive paste (dotite) like the example 1, and all solid state batteries were too produced like the example 1. the place which checked the charge-and-discharge property -- the comparison sample 1-1 of an example 1 -- equivalent initial capacitance characteristics could be checked and it checked that there was no effect of cutting.

[0043] Moreover, when the charge-and-discharge cycle capacity test and the drop test were performed, cycle capacitance characteristics equivalent to a sample 1-1 and the fall engine performance could be checked, and it has checked that it was equivalent to the thing of a large area, and the cycle degradation engine performance was equivalent to the sample of an example 1 in energy density.

[0044] Even if it was the gap where the width of face of processing produced from this with the cell element produced by laser processing is very small, it has checked completely functioning similarly in control of cell expansion contraction and degradation by the impact.

[0045] Processing of the cell element which consists of 90mmx90mm1 piece produced like the <sample 3-2> comparison sample 1-1 was performed using the electron beam within the vacuum chamber. The energy density range is 103 - 109 W/cm². It was processed on conditions. It checked that processing width of face was 0.1-0.5 micrometers by electron microscope observation. It finished setting up the produced cell element in the cel as all solid state batteries like the sample 3-1, and it performed the charge-and-discharge cycle capacity test and the drop test. Consequently, about control of expansion contraction and degradation by the impact, the same effectiveness as a sample 3-1 was checked.

[0046] the <sample 3-3> comparison sample 1-1 -- ** -- processing of the 90mmx90mm cell element produced similarly was performed by electron beam machining like the sample 3-2. It is each area of a cell element 1 micrometer as 0.1 micrometers which is the range which can process processing width of face with an electron beam 2 It was processed. The area with the effective cell element on count corresponds to 82.6% before processing.

[0047] All solid state batteries were produced like the sample 3-1 using this cell element, and charge-and-discharge capacity was measured. a result -- the first stage -- it could check that it was about 80% of 90mm angle by charge-and-discharge capacity, the precision of a processing dimension and capacity was well in agreement, and it has checked that practical use level had the design by dimension convention. Therefore, when it is taken into consideration that there is a limit of the process tolerance of a gap, as for it becoming impossible to secure energy density sufficient as a cell capacity, it is obvious to micrify a cell element more than this, and it is not realistic.

[0048] Therefore, if it be 0.1 micrometers or more as width of face of processing, since propagation of the crack which be in degradation mode inside the cell element by expansion contraction and the impact be intercepted by make into an upper limit width of face of the range which can obtain an effective area as energy density, in the improvement in the cycle engine performance of a cell, it be checked that it be an effective means to mind a very small gap.

[0049] In addition, Li [Li_{0.1} Mn_{1.9}] O₄ which has spinel type structure in this invention, and Li₁/Li [3 Ti₅/3] O₄ Although it used as an active material and 10Li₂ O-25 B-2 O₃-15SiO₂-50ZnO etc. was used as a solid electrolyte, if it is the range which does not deviate from the meaning of invention, various active material ingredients and solid electrolytes can be changed. Moreover, in the processing approach, although processing by laser abb RESSHON was especially used for the example since processing by laser abb RESSHON and dicing was that effective when process tolerance and a mass-production process were taken into consideration, only depending on the width of face of processing, it does not depend for this invention on the approach fundamentally. Therefore, the production approach etc. is not limited to an example, and if it is range which does not deviate from the meaning, it can be changed variously.

[0050]

[Effect of the Invention] As mentioned above, according to all the solid-state rechargeable batteries of this invention, arrange two or more cell elements with a 0.1-5000-micrometer gap, or From arranging two or more cell elements with 5% or less of gap of the total arrangement width of face of this cell element An effective area as energy density can be obtained, and propagation of the crack inside the cell element by expansion contraction and the impact can be intercepted, the electrode crack by the brittle fracture which is the degradation factor of all solid-state rechargeable batteries can be prevented, and cell degradation can be controlled.

[0051] Moreover, according to the manufacture approach of all the solid-state rechargeable batteries of this invention, since this cell element is cut to plurality combining dicing, laser abb RESSHON, chemical etching, plasma etching, ion etching, an electron ray, or these after forming a cell element on a charge collector, the above solid-state rechargeable batteries can be manufactured easily.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to all the solid-state rechargeable batteries that prepared two or more cell elements especially on the charge collector about all solid-state rechargeable batteries.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to all the solid-state rechargeable batteries of this invention, arrange two or more cell elements with a 0.1-5000-micrometer gap, or From arranging two or more cell elements with 5% or less of gap of the total arrangement width of face of this cell element An effective area as energy density can be obtained, and propagation of the crack inside the cell element by expansion contraction and the impact can be intercepted, the electrode crack by the brittle fracture which is the degradation factor of all solid-state rechargeable batteries can be prevented, and cell degradation can be controlled.

[0051] Moreover, according to the manufacture approach of all the solid-state rechargeable batteries of this invention, since this cell element is cut to plurality combining dicing, laser ablation, chemical etching, plasma etching, ion etching, an electron ray, or these after forming a cell element on a charge collector, the above solid-state rechargeable batteries can be manufactured easily.

[Translation done.]

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TECHNICAL PROBLEM

[Description of the Prior Art] Conventionally, as an electrolyte of various cells, although the electrolytic solution of a drainage system or a non-drainage system was generally used, with the demand of thin-shape-izing of the various electronic application devices represented by portable information terminal equipments, such as video photography equipment, a notebook computer, or a cellular phone, and a lightweight miniaturization, it replaces with the above liquefied electrolytes and the solid electrolyte cell using the gel electrolyte which consisted of polymeric materials attracts attention in recent years. Moreover, the various proposals also of the solid electrolyte cell using the inorganic solid electrolyte and the solid polymer electrolyte as an electrolyte are made. By these cells, although it is a solid-state therefore, thin shape-ization is attained by the approach of spreading, a laminating, etc., and positive loading to a pocket device is achieved. Furthermore, all the solid-state rechargeable batteries that formed the electrode active material and the electrolyte with the inorganic compound are also advocated as what can employ efficiently the merit that safety is high and the temperature use range can be taken extensively.

[0003] However, in these all solid-state rechargeable battery, it is fundamentally inherent in the problem of the crack in the electrode which is a sintered compact, or the solid electrolyte which is similarly a sintered compact, i.e., the problem of a brittle fracture. That is, although it is all the solid state batteries that made the inorganic compound sinter therefore, the destruction accompanying expansion contraction of charge and discharge and the destruction accompanying an impact occur. Once a crack arises in large area electrode or solid electrolyte, destruction advances with the generating part as the starting point, soon, destruction will attain to all the whole solid state batteries, and the whole ***** or the whole solid electrolyte ***** will pose a problem with the fatal crack in all solid state batteries.

[0004] Until now, in the rechargeable lithium-ion battery, the device of the relief valve which controls the structure of preventing destruction of sheathing in order to prevent the destruction and breakage, and the run away reaction which occurred inside the cell is advocated. Moreover, also when a cell is damaged completely, the defense mechanism for securing the insurance etc. is advocated. However, about the prevention device of the structure destruction inside a cell, it did not consider as a problem. Moreover, improvement of the active material itself, examination of the mixed ratio of the active material with which expansion contraction differs or examination of the adaptation material to a cell structural member, etc. was performed so that the problem about expansion contraction of the active material accompanying charge and discharge might be seen by JP,5-82131,A, JP,5-159803,A, or JP,6-338321,A as a cure in the system which used nonaqueous electrolyte. And although arranging and producing the septum containing an insulator between the cell elements of all solid-state rechargeable batteries was proposed (for example, refer to JP,5-283055,A and JP,6-215753,A), all were insufficient as a solution over the performance degradation of all the solid-state rechargeable batteries by destruction of a cell element, and there was no protection about the destructive mode of all solid-state rechargeable batteries.

[0005] Like JP,7-122279,A on the other hand, in a solid state battery or a set cell, since the design which establishes space in the interior of a cell is what is a thing aiming at the workability

improvement in the cell which needs terminal strapping etc., or brings about flexibility in order to give cell voltage or the design degree of freedom of capacity by giving wiring on manufacture etc. in the interior of a cell, it is inadequate too from the point of the improvement in energy density. That is, in order to carry to a device or to raise productivity, such a configuration had to be taken, and since many parts which do not contribute to the energy density of a cell directly were included, thing sufficient as energy density was not able to be obtained.

[0006] Therefore, this conventional cell is insufficient as a cell element which does not lower degradation or energy density by destruction.

[0007] It is in this invention being made in view of the above-mentioned trouble, and that 1st purpose preventing property degradation of the cell produced by the brittle fracture by expansion contraction and the impact of the electrode of all solid-state rechargeable batteries, and raising a charge-and-discharge cycle property, and it is in maintaining a high energy consistency in the energy density of a cell as the 2nd purpose, attaining this 1st purpose.

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, all the solid-state rechargeable batteries of this invention arranged said two or more cell elements with the 0.1-5000-micrometer gap in all the solid-state rechargeable batteries that arranged two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and prepared it on the charge collector.

[0009] Moreover, in all the solid-state rechargeable batteries that arranged two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and prepared it on the charge collector, said two or more cell elements were arranged with 5% or less of gap of the total arrangement width of face of this cell element.

[0010] the above-mentioned solid-state rechargeable battery -- each area of said cell element -- 1micrometer² -100cm² it is -- things are desirable.

[0011] Furthermore, by the manufacture approach of all the solid-state rechargeable batteries of this invention, in the manufacture approach of all solid-state rechargeable batteries of preparing two or more positive electrodes which consist of an inorganic compound, solid electrolytes, and cell elements which carried out the laminating of the negative electrode one by one, and formed it on a charge collector, after forming a cell element on said charge collector, this cell element is cut to plurality combining dicing, laser abb RESSHON, chemical etching, plasma etching, ion etching, an electron ray, or these.

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OPERATION

[Function] It is possible to stop the brittle fracture caused with the expansion contraction which all solid state batteries have on the charge collector of all solid state batteries when two or more cell elements are arranged with a very small gap, or an impact in each cell element. Moreover, since the gap is very small, even when it constitutes from many cell elements, it cannot reduce the energy density per the area, that is, can stop the non-donor product to a charge-and-discharge reaction to the minimum, and can form the cell of a high energy consistency.

[0013]

[Embodiment of the Invention] Hereafter, this invention is explained using drawing. The configuration of the cell element in [all] a solid-state rechargeable battery is shown in drawing 1 . The cell element used as the structure into which this inserted the solid electrolyte 2 with the positive electrode 1 and negative electrode 3 of a pair is arranged on the charge collector 5 with the very small clearance 4.

[0014] A positive electrode 1, a negative electrode 3, and a solid electrolyte 2 consist of ingredients shown below, respectively. Namely, as for the active material as an ingredient of electrodes 1 and 3, the chalcogen ghost of transition metals and the transition-metals oxide of Spinel structure are raised. As a chalcogen ghost, TiO₂, Cr₃O₈, and V₂O₅, MnO₂ and CoO₂ An oxide, sulfides, such as TiS₂, and VS₂, FeS, etc. are raised. etc. -- further -- as Spinel structure -- LiMn₂O₄ the various transition-metals oxides represented and the part of those -- various transition-metals oxides, such as an element permutation mold oxide and Li₄Mn₅O₁₂, and the part of those -- an element permutation mold oxide can be used. However, from a viewpoint of the stability of the active material which relates to the cycle engine performance of a cell directly, the active material ingredient of an oxide system is desirable as an active material.

[0015] It is using for a negative electrode 3, respectively what shows more **** potential to a positive electrode 1 for what is not limited especially concerning the selection, compares the charge and discharge potential of two kinds of transition-metals oxides, or a sulfide, and shows electropositive potential more, when using these ingredients as the active material of a positive electrode 1, or an active material of a negative electrode 3, and it is possible to constitute a thing with the cell voltage of arbitration. Furthermore, the need is accepted from the purpose of electronic conductivity assistance, and it is SnO₂. TiO₂ The said conductive additive is mixed and it considers as an electrode material.

[0016] moreover -- the inorganic solid electrolyte 2 used by this invention -- Li_{1.3}aluminum_{0.3}Ti_{1.7}(PO₄)₃ [for example,] Li_{3.6}germanium_{0.6}V_{0.4}O₄ etc. -- a crystalline substance solid electrolyte -- 30LiI-41Li₂O-29P₂O₅ 40 Li₂O-30LiI-35 B-2 O₃-25LiNbO₃, Oxide system noncrystalline solid electrolytes, such as 10Li₂O-25 B-2 O₃-15SiO₂-50ZnO, 45LiI-37Li₂S-18P₂S₅ and 1Li₃PO₄-63Li₂S-36SiS₂ etc., although a sulfide system noncrystalline solid electrolyte etc. can be used It is more desirable to use an oxide system ingredient from the standpoint of the stability of an active material in respect of maintenance of cycle charge/discharge capability ability.

[0017] Next, arrangement of the cell element 6 to a charge collector 5 top is explained. The laminating of each cell element 6 is carried out on the charge collector 5 with the ingredient

mentioned above. It forms by production of a laminated structure being able to form each electrode layer and a solid electrolyte layer by screen-stencil of a up to [sheet forming or a charge collector], making the formed layered product sinter with pressurization heating by the hotpress, and carrying out eburnation. After drying the sheet obtained after applying to the thickness which needs the paste of each electrodes 1 and 3 and a solid electrolyte 2 first with screen-stencil or a doctor blade method in the case of the former sheet forming, it decreases by drying on both sides of a solid electrolyte 2 by the positive/negative two electrodes 1 and 3, and the cell element 6 is produced with a hotpress. furthermore, this production -- a positive electrode 1, the negative electrode 3, and a solid electrolyte 2 -- it is also possible to produce all by screen-stencil or sputtering under an inert atmosphere.

[0018] Similarly the electrode paste carried out with ** forms a solid electrolyte 2 by printing, after performing desiccation and cleaning. Printing and desiccation cleaning of an electrode are further performed after desiccation and cleaning. The cell element 6 is made to sinter with a hotpress first. Then, junction formation of the charge collector 5 is carried out. As a charge collector 5, foils, such as aluminum, gold, nickel, or titanium, can be used.

[0019] Accumulation of the cell element 6 to a charge collector 5 top is producible by calcinating with a hotpress too under an inert atmosphere, or joining with a paste, after installing the cell element 6 produced by the above-mentioned approach to up to a charge collector 5. Moreover, it is also possible to process the configuration and gap which each cell element 6 needs, and to form in them on a charge collector 5, in the electrode of the large area produced by each method of creating previous, with either of the approaches, such as dicing, laser abb RESSHON, chemical etching, plasma etching, ion etching, and an electron ray. Although the gap width of face of processing is producible by any technique as a design, what was especially produced by dicing or laser abb RESSHON is the optimal also in the production configuration and property.

[0020] Moreover, it has a 0.1-5000-micrometer clearance between the cell elements 6. It is impossible in practice from processing being difficult in a gap smaller than 0.1 micrometers. Moreover, it is not realistic too to arrange exceeding 5% to the width of face of the thing and the cell element 6 exceeding 5000 micrometers, when a deployment of a spatial body product is considered. Therefore, as width of face for lowering neither the inter-electrode short circuit prevention after processing, nor energy density, it must be the range of 0.5-1000 micrometers.

[0021] Moreover, as an area of the cell element 6, it is 2 1 micrometer 2-100cm from the absolute magnitude regulated by the precision list of processing from expansion contraction of a crystal. As an area which can use energy effectively from the optimal gap width of face although the range is suitable, it is 2 4 micrometers 2-40cm. It is desirable that it is the range.

[0022] thus, the set cell which carried out accumulation arrangement constitutes a parallel circuit from on the same charge collector, and it becomes possible also for an appearance top and the actual condition the same to operate it as all the solid-state rechargeable batteries of a large area. Therefore, charge-and-discharge actuation whose ***** the charge and discharge current as the aggregate of the cell element 6 according to individual does not have as a cell capacity of all large area independent solid-state rechargeable batteries, either is carried out.

[0023] As shown in drawing 2 , all the solid-state rechargeable batteries that used these cell element 6 processed the positive/negative charge collector, formed the terminal electrodes 7 and 8, and have taken the gestalt covered or packed up by the insulating sheathing 9. Enclosure by thermocompression bonding and covering by resin mold are performed using the laminating complex film of high polymer films, such as polyethylene, polypropylene, or polyester, and aluminum foil as sheathing.

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EXAMPLE

[Example] Next, below, as the solid-state rechargeable battery of this invention was explained in full detail below, it was evaluated.

[0025] (Example 1)

It formed like <sample 1-1> each cell element. It is Li [Li_{0.1} Mn_{1.9}] O₄ as positive active material. It used. as a start raw material -- MnO₂ receiving -- Li₂ CO₃ etc. -- the compound was mixed so that it might become the Li:Mn predetermined mole ratio 1.1:1.9, and it compounded by calcinating in atmospheric air at 450 degrees C - 750 degrees C. It is 30LiI-41Li₂ O-29P₂ O₅ as an inorganic solid electrolyte to 75 % of the weight of this active material. As 15 % of the weight and a conductive auxiliary, weighing capacity of the 10 % of the weight was carried out for ITO (In₂ O₃:SnO₂ = 95:5), and fine particles were fully mixed. The polyvinyl butyral was added 5 % of the weight outside as a binder for shaping to these mixed fine particles, and the paste was prepared for toluene to the solvent using the ball mill. After fabricating the prepared paste in thickness of 100 micrometers and vaporizing a solvent, cleaning of a binder was performed at 350 degrees C, and the electrode was produced through baking in 650-degree C atmospheric air.

[0026] On the other hand, it is Li₁/Li [3 Ti₅/3] O₄ as a negative-electrode active material. It used. as a start raw material -- TiO₂ receiving -- Li₂ CO₃ etc. -- the compound was mixed so that it might become the Li:Ti predetermined mole ratio 4:5, and it compounded by calcinating among atmospheric air at 650-950 degrees C. This negative-electrode active material is used and it is inorganic solid electrolyte 30LiI-41Li₂ O-29P₂ O₅ to 85 % of the weight of active materials as well as a positive electrode. Fine particles were mixed at 15% of the weight of a rate, and negative-electrode mixing fine particles were produced. The binder as well as [as a binder for shaping] a positive electrode was added 5 % of the weight outside to these negative-electrode mixing fine particles, and the paste was prepared for toluene to the solvent using the ball mill. After fabricating the prepared paste in thickness of 80 micrometers and vaporizing a solvent, cleaning and baking of a binder were carried out like the positive electrode, and the electrode was produced.

[0027] Moreover, solid electrolyte 10Li₂ O-25 B-2 O₃-15SiO₂-50ZnO was mixed by the weight ratio 80:20 to the above-mentioned solid electrolyte, 5 weight sections addition of the binder was carried out like the electrode, toluene was used for the solvent, and the paste was prepared. Laminating spreading of the prepared paste was carried out by the thickness of 20 micrometers by screen-stencil on the positive-electrode baking electrode. After carrying out desiccation vaporization of the solvent after applying, degreasing a binder at 350 degrees C among atmospheric air and making three layers into one for a negative-electrode baking object in piles, it is 300 - 600 kgf/cm² with a hotpress. Pressurization baking was carried out at 450-700 degrees C with the pressure. Fabrication of the cell element was carried out to 30mmx30mm by this approach. Between cell elements, accumulation arrangement is carried out to up to the charge collector aluminum of 100mm angle in a 0.5mm gap, similarly nine cell elements produced as shown in drawing 3 are pinched with the charge collector of 100mm angle, and they are 400-600 degrees C and 200 - 600 kgf/cm² under an inert atmosphere. It connected with the charge collector with the hotpress on conditions. The terminal processed the configuration of a terminal

and took out charge collector aluminium foil. The insulation of a charge collector was performed by inserting a resin film. An aluminum lamination is used as sheathing and it is a dew-point. - The cell element was enclosed by thermocompression bonding under the 45-degree C desiccation ambient atmosphere, and ten cels of all solid-state rechargeable batteries were produced.

[0028] The rechargeable battery charging and discharging device performed charge-and-discharge characterization of a cell. After it charged all solid state batteries to 3.5V with the current of 50microA as charge conditions and the electrical potential difference reached 3.5V, charge was suspended and it held for 5 minutes, and after that, it discharged by the discharge current of 50microA to the electrical potential difference of 1.0V, discharge was suspended, it held for 5 minutes, and the charge-and-discharge cycle trial by the repeat of charging to 3.5V was performed again. Five cels were followed in evaluation of the cell engine performance by transition for every cycle of discharge capacity.

[0029] Furthermore, about the five remaining cels produced on the same conditions, whenever it performed 25 cycle charge and discharge, the drop test to the floor line of concrete was performed by making into one unit combination of the direction of the 6th page of the cell which showed all solid-state rechargeable batteries to drawing 3 from height of 50cm. Five every units each of drop tests were performed.

[0030] One cell element was produced to 90mmx90mm by the approach shown by the <comparison sample 1-1> sample 1-1. Similarly ten cels of all solid-state rechargeable batteries equipped with a terminal and sheathing for this cell element like the example 1 were produced. Five cels performed charge-and-discharge cycle measurement like the example, and remainder 5 cel performed the same drop test every 25 cycles. The cycle characteristic test result of a sample 1-1 and the comparison sample 1-1 is shown in drawing 4.

[0031] a sample 1-1 and the comparison sample 1-1 -- in 25 cycle, it was checked both the first stage that the almost same cycle capacitance characteristics are shown. However, although capacity degradation advanced rapidly in the example of a comparison when it went through 150 cycle charge and discharge, as for such degradation, samples 1 and 2 did not happen.

[0032] This is making a cell element small and is because it becomes possible to stop the absolute magnitude of the expansion contraction for every cell element, so decline in the utilization factor inside an electrode is controlled. When the electrode after cycle progress was inspected, peeling of a charge collector perimeter and an electrode was checked in the comparison sample 1. Moreover, when the electrode surface was ground, much particle desorption at the time of nebula or polish was checked by the core and the periphery within the electrode surface, and growth of the defect inside the electrode active material accompanying charge and discharge was supported. The result of a drop test is shown in drawing 5.

[0033] In all the solid state batteries shown in the sample 1-1, capacity degradation by fall was hardly seen. However, by the cell which consisted of one cell element produced by the comparison sample 1-1, what shows extreme capacity degradation from immediately after fall of five units of 25 cycle eye has appeared.

[0034] And by the comparison sample 1-1, the inclination of capacity degradation in the middle of a cycle is also large, and is conjectured that the whole electrode has deteriorated by the charge-and-discharge cycle with the defect as the starting point produced in fall.

[0035] When the cell after a charge-and-discharge cycle was disassembled, in the case of the comparison sample 1-1, compared with the cycle trial which does not fall, much cracks were able to be checked by the result of the cycle trial including fall. Moreover, in the sample 1-1, although there were some which can check much cracks to some cell elements, the crack was not accepted in the other cell element. In order that the defect of a crack with a very small cell element might be shut up in each cell element and might not spread from this to other cell elements by minding a very small clearance, it was checked that the cycle engine performance of all the whole solid state batteries is maintainable.

[0036] As compared with one 90mmx90mm large area, it is clear that the cross section's of all the solid-state rechargeable batteries at the time of being accumulated in the gap exceeding 1.5mm which is 30mm of 5% of cell elements about a cell gap on the other hand energy density carries out 6% or more of fall, and it excepted in the exam.

[0037] (Example 2)

The 30mmx30mm cell element was produced like the <sample 2-1> example 1-1, and ten cells of all solid state batteries too accumulated four cells on up to the charge collector like the example 1 in the 0.5mm gap were produced.

[0038] The 35mmx35mm cell element was produced like the <comparison sample 2-1> sample 2-1, and ten cells of all solid state batteries that accumulated three cells on up to the charge collector like the example 1 in the 0.5mm gap were produced.

[0039] The comparison sample 1 performed the charge-and-discharge cycle trial in the above-mentioned sample 1 list like the example 1. A result is shown in drawing 6.

[0040] By the charge and discharge test to 400 cycles, the capacity is falling to a maximum of about 60% from initial capacity in the comparison sample 2-1 by the sample 2-1 to the capacity variability region being only 80% in an initial capacity factor. Since the area of the cell element to constitute is large about 30%, this is because degradation accelerated more by destruction of the cell element by the expansion contraction accompanying charge and discharge.

[0041] (Example 3)

The cell element which consists of one 90mmx90mm piece like the <sample 3-1> comparison sample 1-1 was produced. The electrode side was fixed to up to a charge collector by heating and pressurization like [while] the example 1. This electrode was fixed in the processing chamber in an atmospheric-air air current, and the electrode by the YAG laser was processed. In processing, they are power density 1 - 106 J/cm². The rate to which the cell element on an X-Y stage is moved was adjusted using the YAG laser of an output, and micro processing was performed. Processing width of face was adjusted with the focus of laser, and processed 9 ****s of cell elements equally. Since laser light reflected in respect of charge collector aluminum, it was able to leave only the charge collector and was able to be processed. It checked after processing that processing width of face was 2-8 micrometers by microscope observation.

[0042] The charge collector was further attached in the cell element after this processing for the charge collector using heating and pressing, or a commercial conductive paste (dotite) like the example 1, and all solid state batteries were too produced like the example 1. the place which checked the charge-and-discharge property -- the comparison sample 1-1 of an example 1 -- equivalent initial capacitance characteristics could be checked and it checked that there was no effect of cutting.

[0043] Moreover, when the charge-and-discharge cycle capacity test and the drop test were performed, cycle capacitance characteristics equivalent to a sample 1-1 and the fall engine performance could be checked, and it has checked that it was equivalent to the thing of a large area, and the cycle degradation engine performance was equivalent to the sample of an example 1 in energy density.

[0044] Even if it was the gap where the width of face of processing produced from this with the cell element produced by laser processing is very small, it has checked completely functioning similarly in control of cell expansion contraction and degradation by the impact.

[0045] Processing of the cell element which consists of 90mmx90mm1 piece produced like the <sample 3-2> comparison sample 1-1 was performed using the electron beam within the vacuum chamber. The energy density range is 103 - 109 W/cm². It was processed on conditions. It checked that processing width of face was 0.1-0.5 micrometers by electron microscope observation. It finished setting up the produced cell element in the cell as all solid state batteries like the sample 3-1, and it performed the charge-and-discharge cycle capacity test and the drop test. Consequently, about control of expansion contraction and degradation by the impact, the same effectiveness as a sample 3-1 was checked.

[0046] the <sample 3-3> comparison sample 1-1 -- ** -- processing of the 90mmx90mm cell element produced similarly was performed by electron beam machining like the sample 3-2. It is each area of a cell element 1 micrometer as 0.1 micrometers which is the range which can process processing width of face with an electron beam 2 It was processed. The area with the effective cell element on count corresponds to 82.6% before processing.

[0047] All solid state batteries were produced like the sample 3-1 using this cell element, and charge-and-discharge capacity was measured. a result -- the first stage -- it could check that

it was about 80% of 90mm angle by charge-and-discharge capacity, the precision of a processing dimension and capacity was well in agreement, and it has checked that practical use level had the design by dimension convention. Therefore, when it is taken into consideration that there is a limit of the process tolerance of a gap, as for it becoming impossible to secure energy density sufficient as a cell capacity, it is obvious to micrify a cell element more than this, and it is not realistic.

[0048] Therefore, if it be 0.1 micrometers or more as width of face of processing, since propagation of the crack which be in degradation mode inside the cell element by expansion contraction and the impact be intercepted by make into an upper limit width of face of the range which can obtain an effective area as energy density, in the improvement in the cycle engine performance of a cell, it be checked that it be an effective means to mind a very small gap.

[0049] In addition, Li [Li_{0.1} Mn_{1.9}] O₄ which has spinel type structure in this invention, and Li₁/Li [3 Ti_{5/3}] O₄ Although it used as an active material and 10Li₂ O-25 B-2 O₃-15SiO₂-50ZnO etc. was used as a solid electrolyte, if it is the range which does not deviate from the meaning of invention, various active material ingredients and solid electrolytes can be changed. Moreover, in the processing approach, although processing by laser abb RESSHON was especially used for the example since processing by laser abb RESSHON and dicing was that effective when process tolerance and a mass-production process were taken into consideration, only depending on the width of face of processing, it does not depend for this invention on the approach fundamentally. Therefore, the production approach etc. is not limited to an example, and if it is range which does not deviate from the meaning, it can be changed variously.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing of the configuration of the cell element of all solid-state rechargeable batteries.

[Drawing 2] It is drawing of the structure of all solid-state rechargeable batteries.

[Drawing 3] It is drawing showing the direction of a drop test of all solid state batteries (one unit).

[Drawing 4] It is drawing of all the solid-state rechargeable battery charge-and-discharge cycle test results of an example 1.

[Drawing 5] It is drawing of all the solid-state rechargeable battery fall cycle test results of an example 1.

[Drawing 6] It is drawing of all the solid-state rechargeable battery charge-and-discharge cycle test results of an example 2.

[Description of Notations]

1 [... A minute gap, 5 / ... A charge collector, 6, 6' / ... 7 A cell element (accumulation arrangement), 8 / ... A terminal electrode, 9 / ... Sheathing] A positive electrode, 2 ... A solid electrolyte, 3 ... A negative electrode, 4

[Translation done.]

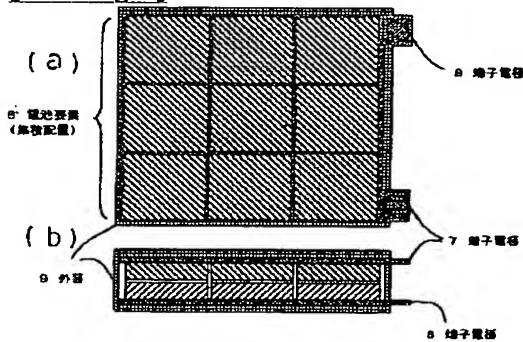
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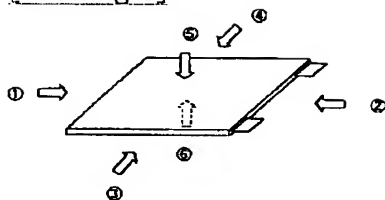
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DRAWINGS

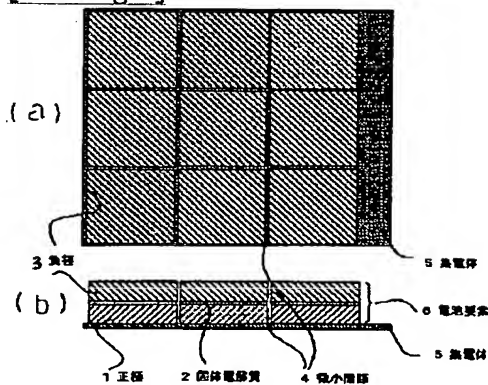
[Drawing 2]



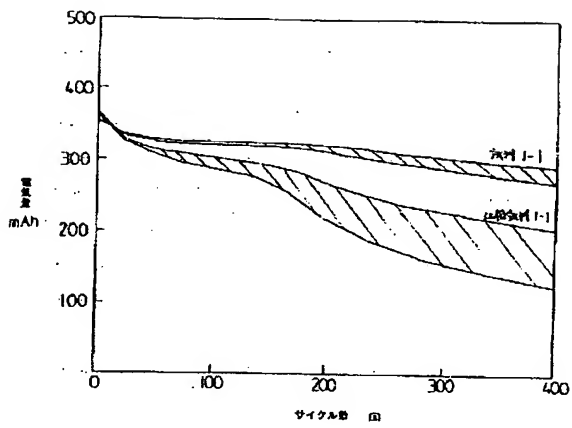
[Drawing 3]



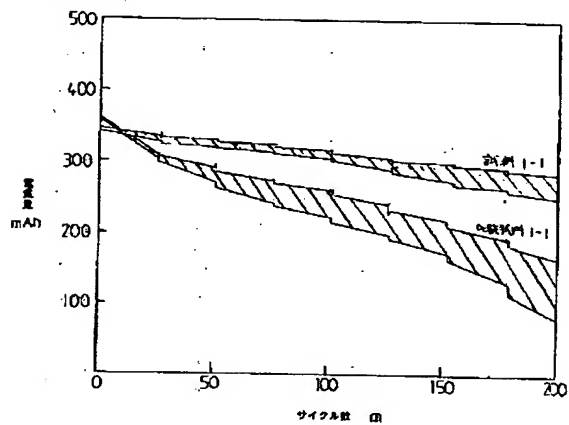
[Drawing 1]



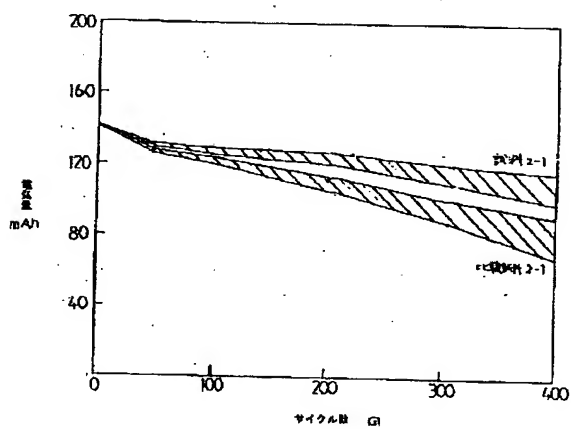
[Drawing 4]



[Drawing 5]



[Drawing 6]



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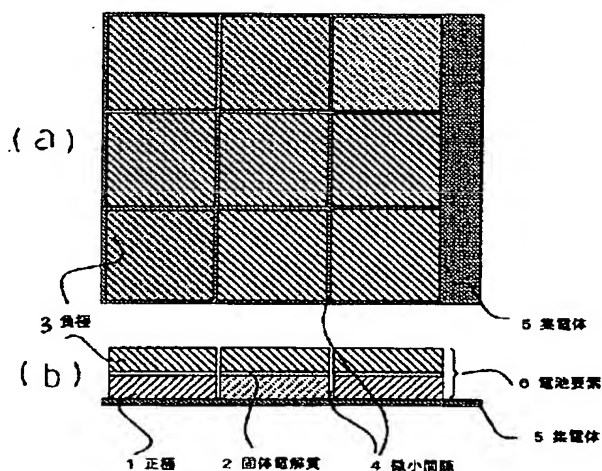
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(54) 【発明の名称】 全固体二次電池およびその製造方法

(57) 【要約】

【課題】 電極の膨張収縮や衝撃による脆性破壊による特性劣化を防止し、充放電サイクル特性を向上させるとともに、高エネルギー密度を維持する。

【解決手段】 無機化合物から成る正極、固体電解質、負極を積層して設けた電池要素を集電体上に複数配設した全固体二次電池であって、上記複数の電池要素を0.1~5000 μ mの間隙をもって配設したり、複数の電池要素をこの電池要素の全配設幅の5%以下の間隙をもって配設する。



【特許請求の範囲】

【請求項 1】 無機化合物から成る正極、固体電解質、および負極を順次積層して設けた電池要素を集電体上に複数配設した全固体二次電池において、前記複数の電池要素を 0.1～5000 μm の間隙をもって配設したことを特徴とする全固体二次電池。

【請求項 2】 無機化合物から成る正極、固体電解質、および負極を順次積層して設けた電池要素を集電体上に複数配設した全固体二次電池において、前記複数の電池要素をこの電池要素の全配設幅の 5%以下の間隙をもって配設したことを特徴とする全固体二次電池。

【請求項 3】 前記電池要素のそれぞれの面積が 1 μm^2 ～100 cm^2 であることを特徴とする請求項 1 または請求項 2 に記載の全固体二次電池。

【請求項 4】 無機化合物から成る正極、固体電解質、および負極を順次積層して形成した電池要素を集電体上に複数設ける全固体二次電池の製造方法において、前記集電体上に電池要素を形成した後、この電池要素をダイシング、レーザーアブレーション、化学エッチング、プラズマエッチング、イオンエッチング、電子線のいずれかもしくはこれらを組み合わせて複数に切断することを特徴とする全固体二次電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は全固体二次電池に関し、特に集電体上に複数の電池要素を設けた全固体二次電池に関する。

【0002】

【従来の技術および発明が解決しようとする課題】従来、各種電池の電解質としては、一般に水系あるいは非水系の電解液が使用されていたが、近年、ビデオ撮影装置、ノートパソコン、あるいは携帯電話などの携帯用情報端末機器に代表される各種電子応用機器の薄型化かつ軽量小型化の要求に伴い、前述のような液状の電解質に代えて、高分子材料で構成されたゲル状の電解質を用いた固体電解質電池が注目されている。また、電解質として、無機固体電解質や高分子固体電解質を用いた固体電解質電池も各種提案されている。これら電池では固体であるがゆえに塗布や積層などの方法で薄型化が可能になり、携帯機器への積極的な搭載が図られている。さらに、電極活物質と電解質とを無機化合物で形成した全固体二次電池も、安全性が高く、温度使用範囲が広範に取れるといったメリットを生かせるものとして提唱されている。

【0003】しかしながら、これら全固体二次電池では、焼結体である電極あるいは同じく焼結体である固体電解質における割れの問題、すなわち脆性破壊の問題を根本的に内在している。つまり無機化合物を焼結させた全固体電池であるがゆえに、充放電の膨張収縮に伴う破壊や衝撃に伴う破壊が発生する。大面積な電極あるいは

固体電解質にひとたび割れが生じると、その発生個所を起点として破壊が進行し、やがては電極全体あるいは固体電解質全体ひいては全固体電池全体へと破壊が及び、全固体電池での割れが致命的な問題となる。

【0004】これまで、リチウムイオン二次電池では、その破壊や破損を防止するために、例えば外装の破壊を防止する構造や、電池内部で起こった暴走反応を制御する安全弁といった機構が提唱されている。また、電池が完全に破損した場合にもその安全を確保するための防御機構なども提唱されている。しかしながら、電池内部の構造破壊の防止機構に関しては問題とされてこなかった。また、充放電に伴う活物質の膨張収縮に関する問題は、非水電解液を用いた系での対策として、例えば特開平 5-82131 号、特開平 5-159803 号、あるいは特開平 6-338321 号などにみられるように、活物質そのものの改善や、膨張収縮の異なる活物質の混合比率の検討、または電池構造部材への適応素材の検討などが行われていた。そして、全固体二次電池の電池要素の間に絶縁体を含む隔壁を配置するなどして作製することが提案されているが（例えば特開平 5-283055 号、特開平 6-215753 号参照）、いずれも電池要素の破壊による全固体二次電池の性能劣化に対する解決策としては不十分であり、全固体二次電池の破壊モードに関する予防策は皆無であった。

【0005】一方、特開平 7-122279 号のように、電池内部に空間を設ける設計は、固体電池あるいは集合電池において、電池内部において製造上配線などを施すことで電池電圧あるいは容量の設計自由度を持たせるために、端子接続などを必要とする電池における作業性改善を目的とするものであったり、柔軟性をもたらすものであるため、エネルギー密度向上の点からはやはり不十分なものである。すなわち、機器へ搭載したり、生産性を上げるためにそのような形状を取らざるを得ないのであり、電池のエネルギー密度に直接寄与しない部分を多く含んでいるため、エネルギー密度として十分なものを得ることができなかった。

【0006】従って、この従来の電池は、破壊による劣化やエネルギー密度を下げない電池要素としては不十分である。

【0007】本発明は上記問題点に鑑みてなされたものであって、その第 1 の目的は、全固体二次電池の電極の膨張収縮や衝撃による脆性破壊によって生じる電池の特性劣化を防止して、充放電サイクル特性を向上させることにあり、第 2 の目的としては、この第 1 の目的を達成しつつ、電池のエネルギー密度において高エネルギー密度を維持することにある。

【0008】

【課題を解決するための手段】上記目的を達成するために、本発明の全固体二次電池は、無機化合物から成る正極、固体電解質、および負極を順次積層して設けた電池

要素を集電体上に複数配設した全固体二次電池において、前記複数の電池要素を $0.1 \sim 5000 \mu\text{m}$ の間隙をもって配設した。

【0009】また、無機化合物から成る正極、固体電解質、および負極を順次積層して設けた電池要素を集電体上に複数配設した全固体二次電池において、前記複数の電池要素をこの電池要素の全配設幅の5%以下の間隙をもって配設した。

【0010】上記固体二次電池では、前記電池要素のそれぞれの面積が $1 \mu\text{m}^2 \sim 100 \text{cm}^2$ であることが望ましい。

【0011】さらに、本発明の全固体二次電池の製造方法では、無機化合物から成る正極、固体電解質、および負極を順次積層して形成した電池要素を集電体上に複数設ける全固体二次電池の製造方法において、前記集電体上に電池要素を形成した後、この電池要素をダイシング、レーザーアブレーション、化学エッチング、プラズマエッチング、イオンエッチング、電子線のいずれかもしくはこれらを組み合わせることで複数に切断する。

【0012】

【作用】全固体電池の集電体上に、微少な間隙をもって複数の電池要素を配置すると、全固体電池の持つ膨張収縮や衝撃で引き起こされる脆性破壊を各電池要素内に留めることが可能である。また、間隙は微少であることから、多数の電池要素で構成する場合でも、その面積当たりのエネルギー密度を低下させることはなく、つまり充放電反応への非寄与体積を最小限に抑えることができ、高エネルギー密度の電池を形成できる。

【0013】

【発明の実施の形態】以下、本発明を図を用いて説明する。図1に全固体二次電池中の電池要素の構成を示す。これは一対の正極1と負極3によって固体電解質2を挟んだ構造となっている電池要素が微少隙間4をもって集電体5上に配設されている。

【0014】正極1、負極3および固体電解質2はそれぞれ以下に示す材料から構成される。すなわち電極1、3の材料としての活物質は、遷移金属のカルコゲン化物やスピネル構造の遷移金属酸化物があげられる。カルコゲン化物としては TiO_2 、 Cr_2O_3 、 V_2O_5 、 MnO_2 、 CoO_2 などの酸化物や、 TiS_2 、 VS_2 、 FeS などの硫化物などが上げられ、さらにスピネル構造としては LiMn_2O_4 に代表される各種遷移金属酸化物、その一部元素置換型酸化物、 $\text{Li}_x\text{Mn}_{1-x}\text{O}_{1.5}$ などの各種遷移金属酸化物、その一部元素置換型酸化物を用いることができる。しかしながら、電池のサイクル性能に直接的に関連する活物質の安定性の観点からは、活物質としては酸化物系の活物質材料が望ましい。

【0015】これらの材料を正極1の活物質あるいは負極3の活物質として用いる場合、その選択に関しては特に限定されるものではなく、2種類の遷移金属酸化物あ

るいは硫化物の充放電電位を比較してより貴な電位を示すものを正極1に、より卑な電位を示すものを負極3にそれぞれ用いることで、任意の電池電圧をもつものを構成することが可能である。さらに、電子導性補助の目的から、必要に応じて SnO_2 や TiO_2 といった導電性の添加物を混合して電極材料とする。

【0016】また、本発明で用いる無機固体電解質2には例えば $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ や $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ などの結晶質固体電解質、 $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$ や $40\text{Li}_2\text{O}_{30}\text{LiI}-35\text{B}_2\text{O}_3-25\text{LiNbO}_3$ 、 $10\text{Li}_2\text{O}-25\text{B}_2\text{O}_3-15\text{SiO}_2-50\text{ZnO}$ などの酸化物系非晶質固体電解質、 $45\text{LiI}-37\text{Li}_2\text{S}-18\text{P}_2\text{S}_5$ 、 $1\text{Li}_3\text{PO}_4-63\text{Li}_2\text{S}-36\text{SiS}_2$ などの硫化物系非晶質固体電解質などを用いることができるが、活物質の安定性の見地から酸化物系材料を用いることが、サイクル充放電性能の維持の点でより好ましい。

【0017】次に、集電体5上への電池要素6の配設について説明する。各電池要素6は上述した材料で集電体5上に積層されている。積層構造の作製は各電極層、固体電解質層をシート成形あるいは集電体5上のスクリーン印刷で形成でき、形成された積層体をホットプレスによる加圧加熱で焼結させて緻密化することで形成する。前者のシート成形の場合、まず各電極1、3ならびに固体電解質2のペーストを必要とする厚みにスクリーン印刷やドクターブレード法で塗布した後、得られたシートを乾燥した後、固体電解質2を正負両電極1、3で挟んで乾燥して脱脂を行ない、ホットプレスによって電池要素6を作製する。さらに、この作製は正電極1、負電極3、固体電解質2すべてをスクリーン印刷や不活性雰囲気下でのスパッタリングで作製することも可能である。

【0018】塗付した電極ペーストは乾燥、脱脂を行った後、同じく印刷で固体電解質2を形成する。乾燥、脱脂の後さらに電極の印刷と乾燥脱脂を行う。電池要素6は、まずホットプレスで焼結させる。その後、集電体5を接合形成する。集電体5としてはアルミニウム、金、ニッケル、あるいはチタンなどの箔を用いることができる。

【0019】集電体5上への電池要素6の集積は、上記方法で作製した電池要素6を集電体5上へ設置した後、不活性雰囲気下でやはりホットプレスで焼成することや、ペーストで接合することで作製できる。また、集電体5上に、先の各作成法で作製した大面積の電極において、個々の電池要素6が必要とする形状と間隙にダイシング、レーザーアブレーション、化学エッチング、プラズマエッチング、イオンエッチング、電子線といった方法のいずれかで加工して形成することも可能なものである。いずれの手法でも加工の間隙幅は設計通り作製可能であるが、とりわけダイシングやレーザーアブレーション

ンで作製したものがその作製形状と特性においても最適なものである。

【0020】また、電池要素6の間は、0.1~5000 μ mの隙間を有する。0.1 μ mより小さい間隙では加工が困難であることから実際上不能である。また、5000 μ mを超えるものや電池要素6の幅に対して5%を超えて配置することは、空間体積の有効利用を考えた場合やはり現実的ではない。従って、加工後の電極間の短絡防止やエネルギー密度を下げないための幅としては0.5~1000 μ mの範囲でなければならない。

【0021】また、電池要素6の面積としては、加工の精度並びに結晶の膨張収縮より規制される絶対量から1 μ m²~100cm²の範囲が適するが、最適な間隙幅からエネルギーを有効に利用できる面積としては、4 μ m²~40cm²の範囲であることが望ましいものである。

【0022】このようにして集積配置した集合電池は、同一の集電体上で並列な回路を構成するものであり、見かけ上も実際も大面積の全固体二次電池と同様の動作が可能となるものである。したがって、個別の電池要素6の集合体としての充放電電流も、大面積単独での全固体二次電池の電池容量としてはそんな色のない充放電動作をするものである。

【0023】これら電池要素6を用いた全固体二次電池は、図2に示すように、正負集電体を加工して端子電極7、8を形成し、絶縁性の外装9によって被覆または梱包された形態をとっているものである。外装としては、ポリエチレン、ポリプロピレン、あるいはポリエステルなどの高分子フィルムとAl箔との積層複合フィルムを用いて、熱圧着による封入や樹脂モールドによる被覆を行っている。

【0024】

【実施例】次に、本発明の固体二次電池を以下に詳述するようにして評価した。

【0025】(実施例1)

<試料1-1>各電池要素のように形成した。正極活物質としてLi[L_{0.1}Mn_{1.9}]O₄を用いた。出発原料としてMnO₂に対してLi₂CO₃などの化合物をLi:Mn所定のモル比1:1.9になるように混合し、450℃~750℃で大気中で焼成することで合成した。この活物質75重量%に対して無機固体電解質として30LiI-41Li₂O-29P₂O₅粉末を15重量%、導電助材としてITO(In₂O₃:SnO₂=95:5)を10重量%を秤量して十分に混合した。この混合粉末に対して成形用バインダーとしてポリビニルブチラールを5重量%外添加し、ボールミルを用いてトルエンを溶剤にペーストの調製を行った。調製したペーストを100 μ mの厚みに成形して、溶剤を揮散させた後、バインダーの脱脂を350℃で行って650℃の大気中での焼成を経て電極を作製した。

【0026】一方、負極活物質としてLi[L_{1/3}Ti_{5/3}]O₄を用いた。出発原料としてTiO₂に対してLi₂CO₃などの化合物をLi:Ti所定のモル比4:5になるように混合し、650~950℃で大気中焼成することで合成した。この負極活物質を用いて正極と同様に、活物質85重量%に対して無機固体電解質30LiI-41Li₂O-29P₂O₅粉末を15重量%の割合で混合して負極混合粉末を作製した。この負極混合粉末に対して成形用バインダーとして正極と同様にバインダーを5重量%外添加し、ボールミルを用いてトルエンを溶剤にペーストの調製を行った。調製したペーストを80 μ mの厚みに成形し、溶剤を揮散させた後、バインダーの脱脂と焼成を正極と同様に実施して電極を作製した。

【0027】また、固体電解質10Li₂O-25B₂O₃-15SiO₂-50ZnOを上記固体電解質に対して重量比80:20で混合し、電極と同様にバインダーを5重量部添加してトルエンを溶剤に用いてペーストを調製した。調製したペーストを正極焼成電極上に、スクリーン印刷で20 μ mの厚みで積層塗布した。塗布した後、溶剤を乾燥揮散させて大気中350℃でバインダーの脱脂を行った後、負極焼成体を重ねて3つの層を一体にした後にホットプレスで300~600kgf/cm²の圧力で450~700℃で加圧焼成した。この方法で電池要素を30mm×30mmに成形加工した。図3に示すように作製した電池要素9個を電池要素間0.5mmの間隙で、100mm角の集電体A1上へ集積配置して同じく100mm角の集電体で挟み、不活性雰囲気下で400~600℃、200~600kgf/cm²の条件でホットプレスで集電体と接続した。端子は集電体アルミニウム箔を端子の形状に加工して取り出した。集電体の絶縁は、樹脂フィルムを挿入して行なった。外装としてアルミニウムラミネートを用い、露点-45℃の乾燥雰囲気下で熱圧着で電池要素を封入して全固体二次電池を10セル作製した。

【0028】電池の充放電特性評価は二次電池充放電装置で行なった。充電条件として50 μ Aの電流で全固体電池を3.5Vまで充電し、電圧が3.5Vに到達した後、充電を停止して5分間保持し、その後、1.0Vの電圧まで50 μ Aの放電電流で放電し、放電を停止して5分間保持し、再度、3.5Vまで充電するという繰り返しによる充放電サイクル試験を行った。放電容量のサイクル毎の推移により電池性能の評価を5セルについて行った。

【0029】さらに、同じ条件で作製した残りの5セルについては、25サイクル充放電を行なう毎に、全固体二次電池を50cmの高さから図3に示した電池6面の方向の組み合わせを1単位として、コンクリートの床面への落下試験を行なった。落下試験は各5単位ずつ行なった。

【0030】＜比較試料 1-1＞試料 1-1 で示した方法で 90mm×90mm に 1 つの電池要素を作製した。この電池要素を実施例 1 と同様にして端子と外装とを備えた全固体二次電池を同じく 10 セル作製した。5 セルは実施例と同様に充放電サイクル測定を行い、残り 5 セルは 25 サイクル毎に同様の落下試験を行なった。試料 1-1、比較試料 1-1 のサイクル特性試験結果を図 4 に示す。

【0031】試料 1-1、比較試料 1-1 共に初期 25 サイクルでは、ほぼ同じサイクル容量特性を示すことが確認された。しかし、充放電 150 サイクルを経過すると、比較例では容量劣化が急激に進行していくが、試料 1、2 とともにそのような劣化は起こらなかった。

【0032】これは、電池要素を小さくすることで、各電池要素毎の膨張収縮の絶対量を抑えることが可能になるため、電極内部での利用率の低下が抑制されるからである。サイクル経過後の電極の検査を行なったところ、比較試料 1 において集電体周囲と電極とのはがれが確認された。また、電極表面を研磨したところ、電極面内で中心部と周辺部に白濁や研磨時の粒子脱離が多数確認され、充放電に伴う電極活物質内部での欠陥の成長が裏づけられた。落下試験の結果を図 5 に示す。

【0033】試料 1-1 に示した全固体電池においては、落下による容量劣化がほとんど見られなかった。しかし比較試料 1-1 で作製した電池要素 1 つから構成された電池では、25 サイクル目の 5 単位の落下直後から極端な容量劣化を示すものが現れている。

【0034】しかも、比較試料 1-1 ではサイクル途中での容量劣化の傾きも大きく、落下で生じた欠陥を起点にして充放電サイクルによって電極全体が劣化していると推測される。

【0035】充放電サイクル後の電池を解体してみたところ、比較試料 1-1 の場合、落下をしないサイクル試験に比べ、落下を含んだサイクル試験の結果では多数の亀裂が確認できていた。また、試料 1-1 においては、電池要素の一部に多数の亀裂が確認できるものがあつたが、それ以外の電池要素においては亀裂は認められなかった。このことから、微少の隙間を介することで、電池要素の微少なクラックといった欠陥が、各電池要素内に閉じ込められ、他の電池要素へと伝播しないために全固体電池全体のサイクル性能が維持できることが確認された。

【0036】一方、電池間隙を電池要素 30mm の 5 % である 1.5mm を超える間隙で集積した場合の全固体二次電池の断面積は 90mm×90mm の断面積 1 枚に比較し、エネルギー密度は 6 % 以上の低下をすることは明らかであり、本試験においては除外した。

【0037】（実施例 2）

＜試料 2-1＞実施例 1-1 と同様に 30mm×30mm の電池要素を作製し、0.5mm の間隙でやはり実施

例 1 と同様に集電体上へ 4 セル集積した全固体電池を 10 セル作製した。

【0038】＜比較試料 2-1＞試料 2-1 と同様に 35mm×35mm の電池要素を作製し、0.5mm の間隙で実施例 1 と同様に集電体上へ 3 セルを集積した全固体電池を 10 セル作製した。

【0039】上記試料 1 並びに比較試料 1 とともに実施例 1 と同様に充放電サイクル試験を行なった。結果を図 6 に示す。

【0040】400 サイクルまでの充放電試験で、試料 2-1 では、その容量変化範囲は初期容量比で 80 % にとどまっているのに対し、比較試料 2-1 においてはその容量は初期容量から最大 60 % 程度にまで低下している。これは、構成する電池要素の面積が 30 % 近く小さくなっていることから、充放電に伴う膨張収縮による電池要素の破壊により、より劣化が加速したためである。

【0041】（実施例 3）

＜試料 3-1＞比較試料 1-1 と同様に 90mm×90mm の 1 個からなる電池要素を作製した。実施例 1 と同様に一方の電極側を加熱・加圧で集電体上へ固定した。この電極を大気気流中の加工チャンパー内に固定し、YAG レーザーによる電極の加工を行なった。加工にはパワー密度 $1 \sim 10^6 \text{ J/cm}^2$ の出力の YAG レーザーを用い、XY ステージ上での電池要素を動かす速度を調節して微細加工を行なった。加工幅はレーザーの焦点で調節し、電池要素を均等に 9 分割加工した。集電体アルミニウムの面ではレーザー光が反射することから、集電体のみ残して加工が可能であった。加工後、顕微鏡観察で加工幅が $2 \sim 8 \mu\text{m}$ であることを確認した。

【0042】この加工後の電池要素へ更に集電体を実施例 1 と同様に加熱・加圧成形あるいは市販の導電性ペースト（ドータイト）を用いて集電体を取り付けて、やはり実施例 1 と同様にして全固体電池を作製した。充放電特性を確認したところ、実施例 1 の比較試料 1-1 同等の初期容量特性が確認でき、切断の影響がないことを確認した。

【0043】また、充放電サイクル容量試験、落下試験を行なったところ、試料 1-1 と同等のサイクル容量特性、落下性能が確認でき、エネルギー密度では大面積のものと同様であり、サイクル劣化性能は実施例 1 の試料と同様であることが確認できた。

【0044】このことから、レーザー加工で作製した電池要素によって作製した加工の幅が微少の間隙であっても、電池膨張収縮および衝撃による劣化の抑制においては全く同じに機能することが確認できた。

【0045】＜試料 3-2＞比較試料 1-1 と同様にして作製した 90mm×90mm 1 個からなる電池要素の加工を真空チャンパー内で電子ビームを用いて行なった。エネルギー密度範囲は $10^3 \sim 10^9 \text{ W/cm}^2$ の条件で加工した。電子顕微鏡観察で加工幅は、0.1～0.

5 μm であることを確認した。作製した電池要素は試料3-1と同様にして全固体電池としてセルに組み上げて、充放電サイクル容量試験、落下試験を行なった。その結果、膨張収縮および衝撃による劣化の抑制に関しては、試料3-1同様の効果を確認した。

【0046】＜試料3-3＞比較試料1-1と同様にして作製した90mm×90mmの電池要素の加工を、試料3-2と同様にして電子ビーム加工で行なった。加工幅を電子ビームで加工できる範囲である0.1 μm として電池要素の各面積を1 μm^2 で加工した。計算上の電池要素の有効な面積は加工前の82.6%に相当する。

【0047】この電池要素を用いて試料3-1と同様にして全固体電池を作製し、充放電容量を測定した。結果、初期の充放電容量で90mm角の約80%であることが確認でき、加工寸法と容量の精度が良く一致し、寸法規定による設計が実用レベルにあることを確認できた。従って、これ以上に電池要素を微小化することは、間隙の加工精度の制限があることを考慮した場合、電池容量として十分なエネルギー密度を確保できなくなることは自明であり、現実的なものではない。

【0048】従って、加工の幅としては0.1 μm 以上であれば、エネルギー密度として有効な面積を得られる範囲の幅を上限として、膨張収縮および衝撃による電池要素内部の劣化モードである割れの伝播が遮断できるため、電池のサイクル性能向上において、微少な間隙を介することが有効な手段であることが確認された。

【0049】尚、本発明においてはスピネル型構造を持つ $\text{Li}[\text{Li}_{0.1}\text{Mn}_{1.9}]\text{O}_4$ 、 $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ を活性物質として用い、固体電解質として $10\text{Li}_2\text{O}-25\text{B}_2\text{O}_3-15\text{SiO}_2-50\text{ZnO}$ などを用いたが、発明の趣旨を逸脱しない範囲であれば活性物質材料および固体電解質は種々変更可能である。また、加工方法においても、加工精度ならびに量産工程を考慮した場合、特にレーザーアブレーションとダイシングによる加工が効果があるものであったためにレーザーアブレーションによる加工を実施例に用いたが、本発明*

*は加工の幅にのみ依存するものであり、その方法には基本的に依存していない。従って、作製方法などは実施例に限定されるものではなく、趣旨を逸脱しない範囲であれば種々変更可能である。

【0050】

【発明の効果】上述したように、本発明の全固体二次電池によれば、複数の電池要素を0.1~5000 μm の間隙をもって配設したり、複数の電池要素をこの電池要素の全配設幅の5%以下の間隙をもって配設することから、エネルギー密度として有効な面積を得られる、且つ膨張収縮および衝撃による電池要素内部の割れの伝播を遮断でき、全固体二次電池の劣化要因である脆性破壊による電極割れを防止し、電池劣化を抑制することができる。

【0051】また、本発明の全固体二次電池の製造方法によれば、集電体上に電池要素を形成した後、この電池要素をダイシング、レーザーアブレーション、化学エッチング、プラズマエッチング、イオンエッチング、電子線のいずれかもしくはこれらを組み合わせて複数に切断することから、上述のような固体二次電池を容易に製造することができる。

【図面の簡単な説明】

【図1】全固体二次電池の電池要素の構成の図である。

【図2】全固体二次電池の構造の図である。

【図3】全固体電池の落下試験方向（1単位）を示す図である。

【図4】実施例1の全固体二次電池充放電サイクル試験結果の図である。

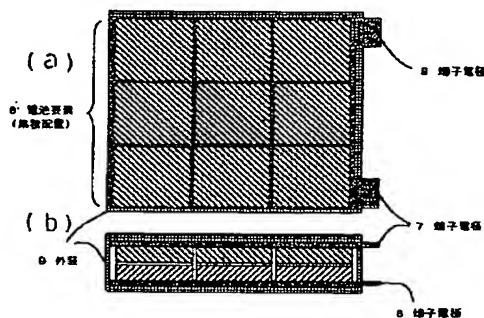
【図5】実施例1の全固体二次電池落下サイクル試験結果の図である。

【図6】実施例2の全固体二次電池充放電サイクル試験結果の図である。

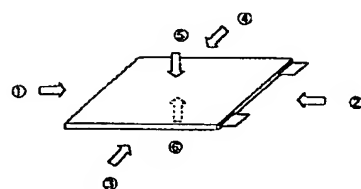
【符号の説明】

1……正極、2……固体電解質、3……負極、4……微小間隙、5……集電体、6、6'……電池要素（集積配置）、7、8……端子電極、9……外装

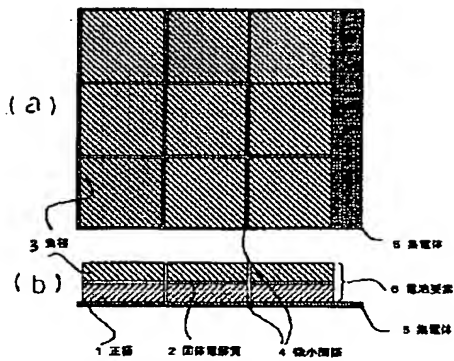
【図2】



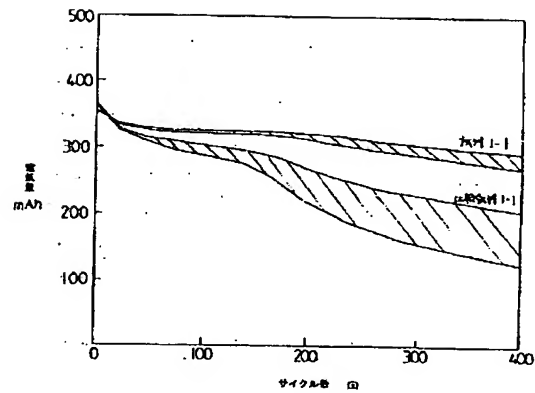
【図3】



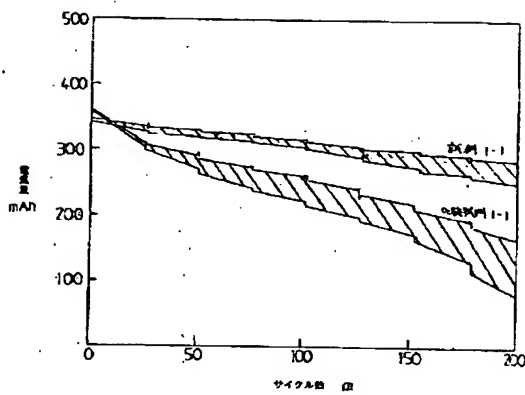
【図1】



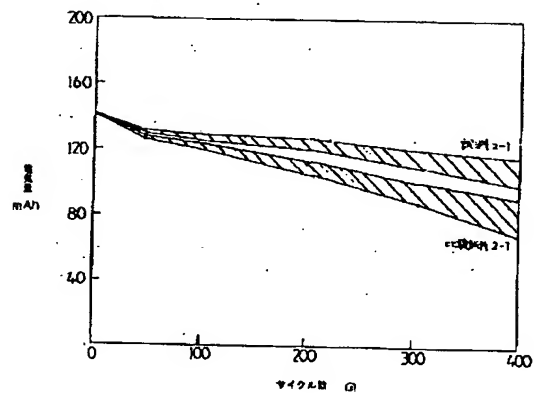
【図4】



【図5】



【図6】



フロントページの続き

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